Metrics for Successful Supercritical Water Oxidation System Operation at the Blue Grass Chemical Agent Destruction Pilot Plant (2019)

DETAILS

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May 1, 2019

Mr. Michael Abaie
Program Executive Officer
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Dear Mr. Abaie:

During a meeting with Mr. Bruce Braun, director, Board on Army Science and Technology, on November 19, 2018, you requested that the National Academies of Sciences, Engineering, and Medicine produce a report proposing some metrics that could be used to judge whether and to what degree the supercritical water oxidation (SCWO) system at the Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP) is meeting its performance goals. You requested that the National Academies form a committee to further develop the material in the 2015 report *Review Criteria for Successful Treatment of Hydrolysate at the Blue Grass Chemical Agent Destruction Pilot Plant*. That report set out criteria for the successful operation of the BGCAPP SCWO system and water recovery system (WRS) and suggested a graded scale to measure the SCWO system performance. The current report uses this scale to develop the metrics and recommendations contained in this letter report.

This study was initiated on January 2, 2019, and had to be completed on an accelerated schedule to support the sponsor's program schedule. In view of the short study schedule and the tightly focused and detailed nature of the task, the National Academies selected committee members with extensive past experience in SCWO, industrial processes, risk and safety assessment, and the destruction of chemical weapons. The Committee on Metrics for Successful Supercritical Water Oxidation System Operation at the Blue Grass Chemical Agent Destruction Pilot Plant was established to accomplish this task. It held a committee meeting on January 14-16, 2019, to receive an in-depth update on the status of the BGCAPP SCWO and WRS systems and then produced this report. The committee roster and biographical information can be found in Attachment A. Report references can be found in Attachment B. A list of acronyms can be found in Attachment C. The acknowledgment of reviewers can be found in Attachment D.

BACKGROUND

The SCWO system is a secondary waste processing reactor that is an important unit in the overall function of the BGCAPP. It is perhaps second in importance behind the agent neutralization reactors, which function to perform base hydrolysis of VX and GB chemical warfare agents. The SCWO system is designed to reactively destroy the primary products of agent hydrolysis, thus preventing chemical reformation of the original agents. This second stage of destruction is mandated by the Chemical Weapons Convention treaty, to which the United States is signatory. The primary products of VX hydrolysis are ethyl, methyl phosponic acid, and di-isopropylaminoethane-thiol and -hydroxide, while the GB hydrolysis products are isopropyl, methyl phosphoric acid, and fluoride. The phosponic acid derivatives in particular display a high level of chemical stability; hence, an aggressive approach is required for their destruction in the hydrolysate product. SCWO provides such an approach.

There has been long-standing concern over the reliable operation of the SCWO system, which is heightened because the SCWO is situated downstream from the agent neutralization reactors, and

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interruptions in the operation of the SCWO have the potential to cause interruptions in or slowing of the chemical weapons destruction processes in the main plant, although a SCWO interruption would have to be very long to cause this. Concern over the operation of the SCWO unit is not rooted in the conceptual ability of the SCWO to destroy organics. It is well documented in the chemical literature that SCWO will function to completely mineralize organics, such as those present in the agent and energetics hydrolysate. However, the very aggressive nature of SCWO will also result in attack on the reactor materials, causing corrosion and cracking, which can compromise the function, and potentially the safety, of the reactor. In addition, the high temperature and pressure required to create and maintain SCWO impose operational demands on components, notably the compressors that are used to pressurize the reactor. Furthermore, measurement devices, like the total organic carbon (TOC) analyzers, are required to function in extreme environments that can degrade their function. Last, the SCWO feed chemistry has been engineered to ensure a eutectic flow of salts in the reactor, preventing buildup on the reactor walls and reactor plugging. This chemistry has been proven in testing. This is discussed in the "A Eutectic Mixture of Salts" section, below. However, if there were an unexpected amount of insoluble compound or particles in the reactors for some reason—say, especially severe corrosion resulting in significant amounts of TiO_2 in the reactor—that could result in augmented corrosion/erosion or reactor plugging.

The concerns discussed above elevate the possibility that the SCWO reactor may not function in a fashion that is compatible with the overall chemical warfare agent destruction rate needed from the BGCAPP main plant. The consequence of this might be that agent hydrolysis would have to be interrupted or slowed, which would occur if the interim storage tanks situated between the agent neutralization reactors and the SCWO system were filled during a prolonged SCWO outage or slow SCWO operations.

If the SCWO were to fail to keep up with the primary agent hydrolysis reactors, then an alternative means for destroying the hydrolysate would need to be identified, such as off-site shipping to a permitted hazardous waste treatment, storage, and disposal facility. Identification of such an alternative for destruction of hydrolysis products would be an involved process, with many factors bearing on any alternative, including efficacy, throughput, safety, treaty compliance, regulatory approval, and public acceptance. Given the challenge of identifying and implementing an alternative, a significant time period would likely be involved, which could delay the destruction of the chemical warfare agent stockpile, prolonging the risk posed by the stored weapons and increasing the safety risk in the eventual destruction, as a consequence of the weapons continuing to age.

BASIS FOR THIS REPORT

The issues and concerns discussed above have motivated multiple studies that have examined the application of SCWO at BGCAPP, and have produced detailed reports describing the operation of the SCWO system and potential problems that might be encountered. The most recent National Academies report was *Review Criteria for Successful Treatment of Hydrolysate at the Blue Grass Chemical Agent Destruction Pilot Plant*, published in 2015 (NASEM, 2015), which identified factors that have the potential to indicate SCWO underperformance. The factors were rated using an arbitrarily assigned value of 0 to 3, which correlated to the success or likely failure of the unit. However, because of the potential consequences associated with identification and implementation of alternatives, a more rigorously defined set of parameters is needed, which can be used to provide a more quantitative evaluation of SCWO performance.

The 2015 report set out criteria for the successful operation of the BGCAPP SCWO system and WRS. The Program Executive Office for Assembled Chemical Weapons Alternatives (PEO ACWA) has requested that the National Academies develop the material in NASEM (2015) to suggest metrics that might be used to determine whether the BGCAPP SCWO system is operating successfully or, if it is not, how great is the likelihood of system failure.

Chapter 6 of NASEM (2015) is titled "Hydrolysate Treatment Criteria for Success and Decision Framework." The chapter contains two elements that are developed in this letter report. First is a set of performance goals for the SCWO and the WRS, broken down into effectiveness goals, cost goals, and schedule goals. This report focuses on the SCWO effectiveness goals and on developing metrics that may be used to determine to what degree these goals are being met.

The SCWO effectiveness goals from NASEM (2015), the sections in which they are considered, and whether metrics were proposed for each individual goal are presented in Table 1.

TABLE 1 SCWO and WRS Effectiveness Goals, Sections in Which They Are Considered, and Whether Metrics Are Proposed

Effectiveness Goal	Report Section	Metrics Proposed
1. Reliably feed agent hydrolysate, energetics hydrolysate, and blended hydrolysate to the SCWO reactors.	Hydrolysate Feed to the SCWO Reactors	Yes
2. Processing rates for SCWO and WRS should be compatible with agent and energetics neutralization processing rates.	Processing Rates, Availability, and Processing Parameters	No
3. Hydrolysates should have a residence time of ≥10 s in reactors at 1,150-1,200°F and 3,400 psig to ensure acceptable destruction of all organic species.	Processing Rates, Availability, and Processing Parameters	No
4. Each SCWO reactor should have a nominal processing rate of 1,000 lb/hr and a target availability of at least 76 percent.	Processing Rates, Availability, and Processing Parameters	Yes
5. To avoid filling the hydrolysate storage tanks, SCWO availability should be no lower than 55 percent.	Processing Rates, Availability, and Processing Parameters	Yes
6. There should be no more than 200 ppm aluminum in blended hydrolysate feed.	Aluminum in Blended Hydrolysate Feed	Yes
7. A eutectic mixture of salts and salt additives should be monitored to ensure that salts remain molten in the SCWO reactor.	A Eutectic Mixture of Salts	No
8. SCWO effluent should meet release specifications for total organic carbon, pH, and conductivity.	Release Specifications for Total Organic Carbon, pH, and Conductivity	Yes
9. Desired time between liner replacement should be at least 300 hr for blended GB hydrolysate and at least 400 hr for blended VX hydrolysate.	Corrosion	Yes
10. Desired time between thermowell replacement should be at least 75 hr for all blended hydrolysates.	Corrosion	Yes
11. Reverse osmosis (RO) permeate for reuse as quench water for SCWO should meet the design objective of ≤500 mg/L total dissolved solids.	Water Recovery System Considerations	No
12. RO reject should contain about 4 wt% salts.	Water Recovery System Considerations	No
13. Sufficient recyclable RO water should be generated to meet SCWO quench water needs.	Water Recovery System Considerations	No

SOURCE: Effectiveness goals found in NASEM (2015, p. 44).

TABLE 2 Graded Success Scale for Use in Evaluating Overall Operation and Individual Treatment Processes

Grade	Definition
0	Success is practically certain (very low probability of SCWO or WRS failure): Operations are proceeding as expected. No BGCAPP actions needed.
1	High likelihood of success (low probability of SCWO or WRS failure): Actions should be taken by BGCAPP to prepare ahead of time for implementation of contingencies in the event of failures. For example, BGCAPP might begin to prepare permit modifications and planning documents.
2	Success is uncertain (moderate probability of SCWO or WRS failure): Actions should be taken to prepare for implementation of contingency operations. For example, BGCAPP might begin processing environmental documentation (permit modifications) and finalizing contingency plans, and begin to initiate changes in infrastructure to permit off-site shipment.
3	Success is unlikely with current operations (high probability of failure of the SCWO or the WRS): Actions are taken to accelerate the implementation of contingency operations and stakeholders are consulted. For example, construction of needed facilities such as new piping and loading docks is completed as quickly as possible; environmental approvals are expedited, if not already obtained; and contracts for shipment off-site and disposal at a permitted treatment, storage, and disposal facility are signed.

SOURCE: NASEM (2015), p. 45.

The NASEM (2015) report also provided a graded success scale for use in evaluating (1) overall operation, and (2) individual treatment processes. The committee uses the scale from NASEM (2015) to develop metrics that show the degree of success of the SCWO system. The scale from NASEM (2015) is reproduced in Table 2.

Chapter 7 of NASEM (2015) is titled “Underperformance and Failure Risks, Systemization, and Contingency Options.” The areas of concern discussed in Chapter 7 include the following (NASEM, 2015):

- Corrosion;
- High-pressure air compressor reliability;
- Compressor condensate oil-water separation operation;
- Liquid effluent letdown valve erosion;
- Solid sulfur heating and mixing in the blend tank;
- SCWO control system code;
- TOC analyzer reliability;
- Preoperational storage;
- Operator currency and experience gaps;
- Unacceptable equipment wear and corrosion during operation;
- Simultaneous maintenance and operation of three reactors, which presents potential safety problems since maintenance personnel would be working near operating reactors;
- Actual agent hydrolysate and energetics hydrolysate successfully tested on smaller SCWO reactors, but only simulated hydrolysates have been tested on a full-scale unit;
- Potential variations in hydrolysate feed composition, which may present operating problems;
- The proper mix of feed additives is complex and is determined using a computer algorithm;
- Elevated aluminum concentrations in the reactor feed may cause reactor plugging; and
- Untested blend tank mixing effectiveness.

Statement of Task

The current Committee on Metrics for Successful Supercritical Water Oxidation System Operation at the Blue Grass Chemical Agent Destruction Pilot Plant was empaneled by the National Academies at the request of PEO ACWA, to address this general objective. The specific objectives of the committee are based on the findings of NASEM (2015) and are detailed in the statement of task, as follows:

- Develop metrics that can be used to determine the success or risks of failure of the BGCAPP SCWO system. These are to be based on the Performance Goals for the SCWO and the WRS, and the Graded Success Scale for Use in Evaluating Overall Operation and Individual Treatment Processes, both in the 2015 report for successful hydrolysate treatment.
- Focus on the parameters of safety; performance; corrosion; and reliability, availability, and maintainability (RAM) and make recommendations for metrics.
- Identify any "no-go" or "stop-work" factors (e.g., safety) that would result in an immediate halt of BGCAPP SCWO operations.

There are many factors that affect the sustainability of SCWO operations, both technical and non-technical. This report only addresses technical factors. In developing the metrics, this letter report focuses on safety, corrosion, performance, and RAM. With sufficient time and funding, any level of underperformance could be tolerated. However, time and funding are not unlimited, and thus there are levels of underperformance below which continued operation of the SCWO may no longer be tenable. An objective of this report will serve to augment the findings of NASEM (2015) in providing more quantitative measures and objective bases for evaluation of SCWO performance to aid PEO ACWA in making these decisions should they prove necessary.

During deliberations, it quickly became clear that it would not be appropriate to simply assign metrics to the performance goals on a one-to-one basis. Rather, the committee decided that, within each topic area as organized along the line of the performance goals, there are only a few operational attributes critical to the successful operation of the SCWO system and, thus, only a few metrics. The committee chose to focus on those attributes having the greatest potential to adversely impact the operation of the SCWO system, so as to avoid diluting the important messages of this report. In all cases, the metrics assume that the SCWO system is operated according to its design basis.

In the two sections "A Eutectic Mixture of Salts" and "Water Recovery System Considerations," the committee determined that there are no useful metrics to propose. In the case of a eutectic mixture of salts, this is entirely in the control of the operators. The necessary chemical recipes have been determined during testing and, so long as they are followed, there will be a eutectic mixture of salts. For the WRS, the committee does not expect this system to impact SCWO operations at all, and so there is no need to propose metrics. Finally, on the topic of safety, it rapidly became clear that this topic is not amenable to treatment by defined metrics. In this case, the committee chose to examine the major safety risks from SCWO operations and maintenance and address how PEO ACWA might best address those risks.

Last, this report is not a system design assessment or analysis. It does not provide a thorough exploration of the system design, design options, and possible failure mechanisms. It is tightly focused on metrics related to the 13 areas laid out in the list of effectiveness goals in Table 1. In doing its work, the committee conducted highly focused data gathering. It then applied its professional expertise and judgment to identify the issues most likely to be a cause for concern and proposed metrics based on those issues. The committee does not provide an opinion on how likely any of these issues might be. It should also be noted that this report relies largely on the committee members' expertise and judgment.

REPORT ORGANIZATION

This report is organized according to the list of 13 effectiveness goals in Table 1. In some cases, a section addresses only one of these goals. In other sections, it made more sense to incorporate more than one goal into the section because these goals formed part of a larger topic (e.g., the "Corrosion" section). In all cases, the goals addressed in a section are clearly specified before the discussion in each section.

Tables 3-7 propose metrics that might be applied to judge the success of SCWO operations, the possible impacts of any difficulties related to those metrics, and an overall assessment of the possible impact to SCWO operations via the graded scale presented in Table 2. The possible impacts of metrics on SCWO operations and their severity are within the specific context of the area that a given table addresses. For instance, different metrics in different tables might be assessed to have a "significant impact." But the significant impact on one table might be short term and readily mitigated, warranting a lesser overall risk assessment via the graded scale. A significant impact on another table might pose a greater overall risk to SCWO operations and thus be given a higher risk rating on the graded scale. Different assessments of possible impacts may rate higher or lower on the overall SCWO success graded scale, depending on the committee's judgment of the high-level, holistic risk presented by each of the individual proposed impacts.

CONSIDERATION OF THE SCWO AND WRS EFFECTIVENESS GOALS

The remainder of this report addresses the following topics:

- A consideration of the effectiveness goals set out in Table 1;
- Proposed metrics that the committee believes will be of most use to PEO ACWA;
- A consideration of safety and stop-work and no-go situations; and
- Findings and recommendations.

Hydrolysate Feed to the SCWO Reactors

This section addresses goal 1 in the list of effectiveness goals in Table 1. The committee interprets this to encompass both the ability to mechanically feed hydrolysate reliably and the ability to feed chemically appropriate hydrolysate (i.e., there are both mechanical and chemical components). The feed and blending system portion of the overall SCWO system has been designed to meet the target feed rates and conditions set by the operation parameters of the SCWO reactors. Equipment testing and shakedown will be part of the commissioning process where any identified equipment or system limitations can be determined and addressed. Operating and analytical procedures, such as established chemical recipes and sample testing, have been developed to ensure that the blended hydrolysate feed to the SCWO meets specifications. At this writing, it is not known what the SCWO tolerance level is to variability in the composition of the blended hydrolysate feed streams. The validity of the blending procedures, including additive supply to the blend tank, will need to be verified during commissioning. If the recommendations below are met, the performance metric of meeting feed specifications and reliably supplying this material to the SCWO during actual operations should be achievable and should, therefore, not impact meeting the overall performance goal of destroying hydrolysate.

While the conditions under which hydrolysate will be transported from storage to the reactor are clearly less aggressive than in the reactor, it would be useful to examine the durability and reliability of distribution lines during the planned test period. The planned testing using water, then surrogate, followed by hydrolysate provides a means of making such an evaluation. Nondestructive inspection approaches (such as ultrasonic testing, eddy current testing, perhaps X-ray tomography) could be used during this testing to assess wall thinning or other modes of corrosion that may occur. The committee proposes some metrics for this in Table 3.

TABLE 3 Proposed Metrics for Reliable Hydrolysate Feed to the SCWO Reactors

Graded Scale	Definition	Performance	RAM
0	Feed chemistry and corrosion are as expected.	No impact	No impact
1	Feed chemistry has minor variations from expected composition.	Minimal impact	Minimal impact
1	Corrosion in feed piping with actual hydrolysate is slightly higher than anticipated.	Minimal impact	Minimal impact
2	Feed chemistry is significantly off-spec.	Significant impact	Significant impact
2	Corrosion of feed piping is higher than expected and affects only pipe integrity.	Significant impact	Significant impact
2	Feed chemistry is sufficiently off-spec to disrupt operations—for example, problems with salt formation.	Significant impact	Significant impact
2	Corrosion is sufficient to cause equipment failure, affect feed chemistry, or contribute significant solid particle loading.	Significant impact	Significant impact

Finding 1. Commissioning, startup, and the beginning of actual operations will provide many opportunities to take measurements of SCWO system performance.

Recommendation 1. During commissioning, startup, and the beginning of actual hydrolysate operations, BGCAPP staff should take every opportunity to make actual measurements of SCWO system performance to identify any issues that may be developing rather than relying on previous test results.

Finding 2. Equipment and system limitations may become apparent during commissioning that may affect the ability to reliably feed blended hydrolysate to the SCWO system.

Recommendation 2. BGCAPP staff should identify equipment and system limitations during commissioning that would affect SCWO feed and address them.

Finding 3. Blending procedures for the SCWO feed need to be validated and the tolerance to variability in the chemical composition of the SCWO feed need to be determined.

Recommendation 3. BGCAPP staff should both verify the validity of the blending procedures, including additive supply to the SCWO feed blend tank, and determine the SCWO tolerance level to variability in the composition of the blended hydrolysate feed streams.

Processing Rates, Availability, and Processing Parameters

This section addresses goals 2-5 in the list of effectiveness goals in Table 1.[1] Experimental operation of the SCWO reactor has demonstrated that acceptable destruction of all organic species can be achieved if the reactor system is operated at 1,150-1,200°F and 3,400 psig with a feed residence time in the reactor of 10 s or more. This temperature range, pressure, and residence time are part of the design basis, and thus

[1] "Availability" refers to the proportion of time, in this context a percentage, that the SCWO reactor is available for routine operations. An availability of 76 percent, for example, would mean that the reactors are available for operations 76 percent of the time and are off-line for maintenance, or some other reason, 24 percent of the time.

the supporting equipment has been designed to meet these conditions. There will be a commissioning and testing period prior to agent hydrolysate processing.[2] This trial period represents an appropriate time period to confirm this capability. That being said, there is no expected impact related to these conditions, as they are very likely to be met absent unexpected problems not similar to anything encountered in testing.

To accomplish its mission, the SCWO system processing rates must be sufficient to allow the volume of energetics and agent hydrolysate produced from the main plant to be treated in a timely manner to avoid an exceedance of hydrolysate storage capacity. Such an exceedance would impact main plant operations. The SCWO processing rate does not need to match the hydrolysate production rate, as storage capacity for hydrolysate exists to allow for a finite level of inventory build. However, if the SCWO process rate falls to a level where the storage capacity will be exceeded with no likelihood of any catch-up while main plant operations are paused during agent campaign changeovers, the impact to the successful neutralization of agent inventory will be significant. The nominal design processing rate for each SCWO train is 1,000 lb/hr of material at an overall SCWO processing building availability of 76 percent (i.e., 76 percent across all three SCWO trains). With three trains in the facility, this design capacity exceeds the processing requirements to meet treatment objectives. Data gathering at the January 2019 meeting indicated that processing rates with two trains operating at 55 percent would be sufficient, although only barely, to meet expected main processing plant production.[3] The 55 percent target availability is also referenced in Box 6.2 of NASEM (2015). Thus, it can be concluded that if the operating rates of three trains meet or are even close to design rates, the impact on the overall processing capability will be low. Put another way, if individual SCWO train availability is greater than 55 percent, the impact on the destruction of chemical inventory will be low. Table 4 proposes some metrics in this area.

Finding 4. The overall SCWO processing building availability rates are expected to be sufficient to not impact main plant operations.

TABLE 4 Proposed Metrics for Processing Rates, Availability, and Processing Parameters

Graded Scale	Definition	Performance	RAM
0	All three trains run with a feed rate of 1,000 lb/hr and availability of 76 percent.	No impact	No impact
1	All three trains run with a feed rate of 1,000 lb/hr and an availability of between 55 and 76 percent.	Minimal impact	Minimal impact
1	Two of three trains demonstrate a feed rate of 1,000 lb/hr and an availability greater than 60 percent.	Minimal impact	Minimal impact
2	No more than one train is able to demonstrate 1,000 lb/hr and availability greater than or equal to 55 percent.	Significant impact	Significant impact

[2] G. Lucier, deputy chief scientist, BGCAPP, "SCWO Systemization Phase Strategy Update," presentation to the Committee on Chemical Demilitarization, October 16, 2018.
[3] G. Lucier, deputy chief scientist, BGCAPP, "Supercritical Water Oxidation (SCWO) Update Briefing," presentation to the committee, January 14, 2019.

Aluminum in Blended Hydrolysate Feed

This section addresses goal 6 in the list of effectiveness goals in Table 1.[4] The performance goal of ≤200 ppm of aluminum in the blended hydrolysate feed stems from issues with the formation of aluminum hydroxide precipitates in the SCWO reactor and downstream high-pressure effluent heat exchanger. Excessive aluminum levels could result in salt plugs and reduce SCWO system availabilities, by causing plugging of the SCWO reactors or scaling on the heat exchangers. Potential sources of high aluminum in the SCWO feed include a mechanical malfunction of the aluminum precipitation system (APS) and the aluminum filtration system (AFS) and a pH that is out of the specified range for APS and AFS operations.

Most of the aluminum in the raw feed is found in the energetics hydrolysate. The APS and the AFS will treat the energetics hydrolysate and are expected to reduce the aluminum concentration to 2 ppm.[5] Some of the aluminum in the SCWO feed is found in the GB agent hydrolysate, since the GB agent is slightly corrosive to the aluminum warheads. The agent hydrolysate will not be pretreated, but data in a SCWO Working Group report suggests that the highest aluminum amount previously found in GB from rocket warheads is below that of concern for solids accumulation in the SCWO system (BPBGT, 2014).[6]

In its 2014 report, *Recommendations for Correcting Potential Gaps in Supercritical Water Oxidation (SCWO) Knowledge, Experience, and Performance*, the SCWO Working Group developed a list of 33 recommendations to address critical deficiencies that needed to be addressed for safe and effective SCWO operations. Two of these recommendations address the issue of aluminum, as follows (BPBGT, 2014, pp. 10-11):

- Recommendation 3.10: Develop and certify analytical methods for the 6 elements of interest (Na, S, Cl, P, F, and Al) using genuine hydrolysate samples from bench-scale synthesis.
- Recommendation 3.27: Ensure the profile for Lab analysis of blended hydrolysate includes aluminum, specific gravity, and pH.

While both of these actions aid in achieving the target aluminum concentration in the SCWO feed, the committee has one concern—namely, that protocols developed for bench scale synthesis of hydrolysate-simulant feed used for SCWO testing may not scale properly to the generation of blended hydrolysate that will ultimately be used in the larger SCWO blend tank. It is possible that the agent and energetics hydrolysates that comprise the blended hydrolysate feed may exhibit inconsistent mixing that might lead to locally higher aluminum concentrations.

Factors that will mitigate aluminum in the APS and AFS were identified by the SCWO Working Group. These include the following (BPBGT, 2014):

- The APS/AFS system (if operating correctly) will reduce the aluminum in energetics hydrolysate below levels of concern.
- The accuracy of readings by pH probes will be ensured by parallel probes reading within 0.5 pH units of each other. Monitoring and control of pH is critical to the safe and effective operation of the APS/AFS system. While redundant pH probes will help accuracy, there does not appear to be any safeguard against both probes systematically reading high or low based on a common problem.

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[4] After the report had been completed, PEO ACWA decided to not use the BGCAPP Energetics Neutralization System. This change both eliminates the dominant source of aluminum to the SCWO feed and eliminates the aluminum precipitation system and the aluminum filtration system. The report does not reflect this change.

[5] Ibid.

[6] The SCWO Working Group consists of a system contractor and PEO ACWA staff who report to the PEO ACWA on matters related to the SCWO system.

- The throughput of the APS/AFS system appears to be approximately twice that needed to operate all three SCWO trains simultaneously. This matters because the overcapacity of the APS/AFS system would enable the system to function in the middle of its operational range, and excursions in the Al concentration of the feed are not likely to stress the system.

The SCWO Working Group further identified a design mitigation factor and an operational mitigation factor to address aluminum concerns. The design mitigation is an on-line spare for the high-pressure effluent heat exchanger. Thus, if one heat exchanger becomes plugged due to high aluminum concentrations in the SCWO feed, the spare can be brought on-line to allow the SCWO system to keep operating and repairs to be made during the next scheduled maintenance outage. The operational mitigation factor is the planned aluminum analysis of every blend tank batch, which will provide "a basis for forensic analysis."[7] A concern of the committee is the possibility that the aluminum analysis will not be a standard preoperational check to help prevent high aluminum feed from being processed. The use of the word "forensic" seems to indicate analysis after the fact. It is important that accurate aluminum testing is an explicit part of their standard preoperational checks prior to the processing of every blend tank batch. Further, it is unclear to the committee that a plan exists to reduce the aluminum concentration in the agent hydrolysate should it be found to be too high. Table 5 proposes some metrics in this area.

Finding 5. A plan to address unexpectedly high aluminum levels is important to mitigate the risks of unexpected problems to SCWO operations.

Recommendation 4. If one does not already exist, BGCAPP staff should prepare a plan to mitigate high aluminum concentrations in the SCWO feed should it prove necessary.

TABLE 5 Proposed Metrics for Aluminum Concentrations in Hydrolysate

Graded Scale	Definition	Safety	Performance	RAM
0	Aluminum level is reliably maintained in all blended hydrolysate feed batches.	No impact	No impact	No impact
1	Average aluminum level is 200-300 ppm 90 percent of the time.	Minimal impact because of safety redundancies in system.	Minimal impact to organic conversion rates.	Minimal impact to RAM but maintenance time may be increased to clean out aluminum precipitate.
2	Average aluminum level is >300 ppm most of the time.	Increased safety risks due to potential plugging of safety features (pressure relief valves).	Minimal impact to organic conversion rates.	Increased impact to RAM due to increased maintenance time and downtime.
3	Aluminum level spikes to >500 ppm for individual batches.	Stop-work/no-go. Need to resolve cause of higher Al levels and mitigate before feeding these blend batches.	Potential for some impact on organic conversion rates if organics bind with aluminum precipitates.	Significant impact on RAM until problem is resolved.

[7] G. Lucier, deputy chief scientist, BGCAPP, "Supercritical Water Oxidation (SCWO) Update Briefing," presentation to the committee, January 14, 2019, p. 24.

A Eutectic Mixture of Salts

This section addresses goal 7 in the list of effectiveness goals in Table 1. The formation of molten eutectic salt flows in the SCWO reactor is important for two reasons. First, it prevents salt clogging of the reactors. Second, the molten flows coat the SCWO liners and provide some protection from erosion from the aggressive SCWO environment. Chemicals will be added to the SCWO feed to ensure the creation of these molten flows. Current plans are to monitor salt composition of the SCWO feed before and after the addition of chemicals to confirm that the resulting chemistry is appropriate for feeding to the SCWO. This monitoring, upstream of the SCWO, is vital to ensure that the salts in the SCWO feed form a molten protective coating of the SCWO reactor liner, as designed, and remain as such without salt plugging of the reactors. Each agent campaign, GB and VX, has its own specific recipe.

NASEM (2015) discusses this concern in depth. Any degradation of the eutectic mixtures and molten coating could result in decreased SCWO availabilities due to the need to spend more time than planned clearing salt plugs or replacing liners more frequently due to increased corrosion. The impact of salt plugging could be more severe, perhaps ultimately requiring the replacement of a reactor or associated appurtenances if severe enough.

From extensive chemical and system testing, the eutectic composition has been specified as a 2:1 ratio of $NaCl:Na_2SO_4$, and no information regarding the sensitivity of the eutectic to variations in this ratio was provided to the committee, nor was information provided on the effect of variations in the additives. The committee noted during its January 2019 meeting that the concentrations of additives to the SCWO feed are specified out to three decimal places—a tenth of a percent.[8] It is unlikely that the formation of the eutectic will be sensitive to such small variations in the feed composition. However, the relationship between feed composition variations and eutectic formation does not appear to be explicitly known. It would be useful to understand additive concentrations beyond which the formation of the eutectic is adversely affected. This would enable establishment of control values for bounding feed composition, which could include consideration of precision, thereby justifying the precision (significant figures) currently imposed on the additives to the SCWO feed.

Finding 6. There does not appear to be any information on the relationship between variations in additive feed concentrations and eutectic formation.

Recommendation 5. During testing with water and simulants, BGCAPP staff should establish the relationship between variations in additive feed concentrations and eutectic formation, including determining the sensitivity of eutectic formation to variation in the concentrations of feed additives.

Release Specifications for Total Organic Carbon, pH, and Conductivity

This section addresses goal 8 in the list of effectiveness goals in Table 1. The permit level for TOC in SCWO effluent is 50 ppm and, as long as the SCWO reactor operating conditions are maintained within target ranges, this criterion will be met. Operational verification that the system is meeting this target will be accomplished using on-line TOC analyzers, two on each reactor train.[9] During development and first-of-a-kind (FOAK) SCWO testing, the reliability of these analyzers was less than desired. Issues with the analyzers included interferences with sample supply and, therefore, unreliable TOC performance data for SCWO operation. Design fixes have been implemented in the sample supply mechanism but will be tested only after the units are started up in BGCAPP. As a result of the analyzer performance during

[8] G. Lucier, deputy chief scientist, BGCAPP, "Supercritical Water Oxidation (SCWO) Update Briefing," presentation to the committee, January 14, 2019, p. 21.

[9] On-line sensors are attached to the system and take samples from the flow. In-line sensors are directly in the process flow.

FOAK testing, design changes were identified and have been incorporated as part of 33 critical deficiency issues that are being addressed by the SCWO Working Group.[10] If the TOC specification is not met, the SCWO product water is diverted to an off-spec storage tank. The likelihood of not meeting the TOC specification during proper SCWO operation and, therefore, the impact on the system's ability to meet process requirements, is low. However, if the TOC analyzers are not adequately reliable, it may not be possible to verify that the TOC specification has been met, which will negatively affect SCWO operations.

Generally, to negatively impact SCWO operation the TOC analyzers would have to suffer an availability that is lower than the required SCWO operational availability. Since each SCWO train has two analyzers, the criticality of an individual analyzer is diminished. As long as one analyzer on each train is available during operation and providing data to confirm SCWO performance, this will allow the SCWO to continue processing hydrolysate. Because of the redundancy in TOC analyzers, the impact of analyzer problems on the SCWO operation would be minimal so long as one analyzer is available at all times. The maintenance requirements of the analyzers to sustain that operation, however, could be significant.

In the event that the on-line TOC analyzers do not provide the on-line time to successfully meet processing requirements—that is, contributing to less than 55 percent overall SCWO availability—an alternative methodology to validate the TOC levels of the effluent to meet specifications could reduce any impact on SCWO operations. One such alternative is an appropriate manual sampling program at a frequency to keep SCWO production levels at the 55 percent availability level discussed in the "Processing Rates, Availability, and Processing Parameters" section. In the event of problems with the TOC analyzers, the impact on the SCWO availabilities without this approach will be high.

Finding 7. Having a backup plan in case the TOC analyzers do not work as needed would mitigate a potential risk to SCWO operations.

Recommendation 6. In light of previous issues with total organic carbon (TOC) analyzer reliability, BGCAPP staff should develop a backup manual TOC analysis methodology to allow SCWO operations to continue in case of TOC analyzer underperformance.

The SCWO effluent will be further processed through the WRS to recover water that will then be used as quench water within the SCWO system. This quench water is required to meet pH and conductivity requirements to be suitable for this use. Since the WRS includes water conditioning, filtration, and an RO system, the pH of the effluent will be controlled within acceptable ranges, and the conductivity will be very low due to the characteristics of RO permeate from the WRS. Thus, with a properly operating WRS, the recycled quench water will meet these specifications, and as long as the WRS is able to operate properly, there will be no impact on the availability of the SCWO system due to off-spec quench water. Table 6 proposes some metrics in this area.

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[10] G. Lucier, deputy chief scientist, BGCAPP, "The BGCAPP Implementation of SCWO," presentation to the committee, January 14, 2019.

TABLE 6 Proposed Metrics for Release Specifications for TOC, pH, and Conductivity

Graded Scale	Definition	Performance	RAM
0	All TOC analyzer systems function effectively and provide timely confirmation of less than 50 ppm TOC in the effluent.	No impact	No impact
0	All TOC analyzers have an availability that matches the SCWO reactor availability and thus provide timely data while the SCWOs are operating.	Minimal impact	Minimal impact on availability requirements; significant impact on analyzer maintenance
1	During operation each train is able to keep one analyzer operational to confirm processing performance, thereby confirming effluent TOC content in a timely manner.	Minimal impact	Minimal impact on availability requirements; significant impact on analyzer maintenance
2	All TOC analyzers demonstrate an availability significantly lower (<50 percent availability) than the SCWO reactor trains.	Would have significant impact unless manual sampling and analysis procedures can be developed to meet SCWO performance requirements	Significant impact

Corrosion

This section addresses goals 9 and 10 in the list of effectiveness goals in Table 1. At the time this report was written, the design/build/systemization stage of the BGCAPP facilities was nearing completion. The next phase, which involves staged preoperational testing using water, surrogate, and ultimately actual hydrolysate operation for 6 months, allows a determination of the performance of the materials of construction and verification of expected corrosion behavior in service conditions.

The corrosion rates expected for the BGCAPP SCWO reactors are based on measurements made during FOAK testing. Measurements were made at local positions where corrosion was observed during the examination of the liner. The extent of corrosion varies at different liner positions (NRC, 2013). Liner lifetime will be dictated by the extent of corrosion measured at local positions where the extent of corrosion is the greatest, typically in the upper portion of the SCWO reactor. Liner inspections will emphasize the identification of places where the most corrosion has occurred. Failure to meet expected corrosion rates for the titanium liners and thermowells in the SCWO reactor established during FOAK testing, which were used to inform the system design and are summarized in NRC (2013), will impact the operational efficiency and safety of the SCWO system.

Titanium liner corrosion and thermowell erosion corrosion have been identified as important limiting issues in the SCWO system (NRC, 2013). At this point, thermowell corrosion is expected to determine the maximum operating time between reactor shutdowns and maintenance. The observed corrosion rates of the liner and thermowells have been measured to be on the order of 1 mil/hr. The corrosion rates are greater for higher temperatures and flow rates (as high as 1.9 mil/hr) and less for lower temperatures and flow rates. The corrosion damage has the appearance of erosion-corrosion, which is a phenomenon whereby the damage is much greater than would be the case for either erosion or corrosion alone. Erosion reduces the effectiveness of the protective layer that forms on corrosion-resistant materials, permitting the corrosion reaction to progress faster than expected. This may at least partially explain why the observed attack is greatest at the top of the reactor, where the flow is most turbulent and hence most erosive. Lower in the reactors, the flow pattern may be nearer to laminar flow, which is much less erosive. The presence of liquid salts on the reactor wall lower in the reactor may also contribute to the lesser damage rate by providing a physical barrier between the reactor wall and its contents. The maximum allowable extent of corrosion prior to liner replacement is 67 percent of the initial liner wall thickness (33 percent remaining) and 80 percent for the thermowells (20 percent remaining) (NRC, 2013). Thermowell and liner replacement both require shutdown of the SCWO reactor, and total downtime is about 6-7 hr for thermowell replacement and 10-12 hr for liner replacement (NRC, 2013). Corrosion is expected, and it appears that the corrosion rates are predictable and that replacement can be treated as a maintenance issue rather than as an equipment failure (NASEM, 2015). Nevertheless, the frequency of replacement will still have an effect on reactor throughput (performance) and will need to be monitored continuously.

While the conditions under which hydrolysate will be transported from storage to the reactor are clearly less aggressive than those on the critical path to operation in the reactor, they are still aggressive enough to present corrosion concerns. It would be useful to examine the durability and reliability of distribution lines during the planned test period. The planned testing using water, then surrogate, followed by actual hydrolysate provides a means of making such an evaluation and is discussed in the next two sections. This is also treated in the “Hydrolysate Feed to the SCWO Reactors” section, above.

Liner Replacement

This section addresses goal 9 in the list of effectiveness goals in Table 1. In the current operational protocol, the desired time between liner replacements is considered to be at least 300 hr for blended GB hydrolysate and at least 400 hr for blended VX hydrolysate. NRC (2013) supported the 300 hr liner change-out interval recommended for the operational GB hydrolysate campaign as adequate if the operating temperature remains at the recommended 1,150°F and the flow rate is 1,000 lb/hr. On the other hand, that assessment concluded that the 400 hr liner change-out interval recommended for the VX nerve agent campaign is not supported by the worst-case corrosion data given in NRC (2013). NRC (2013) recommended that BGCAPP shorten the liner change-out period for VX processing from the 400 hr proposed in the test report until the corrosion rates under actual operating conditions are verified and suggested that 200 hours would be a better initial change-out period.

This committee is not aware of what consideration might have been given by BGCAPP to the NRC (2013) recommendation regarding liner change-out, but that report adds emphasis to this committee’s view that final liner replacement decisions be supported by verification of corrosion rates under operating conditions. The planned testing using water, then surrogate, followed by actual hydrolysate is a means of addressing that recommendation. Each stage of the planned testing presents an opportunity to examine the performance of the liners. For example, testing with water will allow a baseline evaluation of the liner corrosion rate and mode of corrosion through the removal of the liners at multiple 300 and 400 hr intervals to allow examination. Similarly, examination at the same intervals during operation with hydrolysate surrogates would determine how the liner responds to a more aggressive medium. Last, determination of the corrosion rate and mode of corrosion at the same multiple intervals with blended GB and VX hydrolysate would provide a verification of the kind recommended in NRC (2013). It also bears mentioning that if liner replacement is required more frequently than expected, workers would be exposed more frequently to the hazards identified in the “Safety, Risk Assessment, and Risk Management” section of this report.

Finding 8. There will be many opportunities during SCWO testing and early operations to validate expected corrosion rates through direct measurements.

Recommendation 7. BGCAPP staff should perform actual measurements of liner corrosion during testing with water, with hydrolysate surrogates, and during actual agent operations. Evaluations should involve a determination of wall thinning and metallographic examination for local corrosion modes (pitting and cracking in particular). An assessment of the effect of molten salt flow from the perspective of erosion and corrosion and the effectiveness of corrosion control additives should also be part of this systematic evaluation prior to full-scale operations.

Thermowell Replacement

This section addresses goal 10 in the list of effectiveness goals in Table 1. Thinning of the thermowells (accompanied by mechanical failure when minimal material remains) is expected to be the most frequent maintenance issue associated with continuous operations (NRC, 2013). NRC (2013) recommended that the diameter of the thermowells should be increased to at least 0.75 in. from the current diameter of 0.50 in. by increasing the wall thickness. The committee that authored NRC (2013) considered this operation a simple modification that would lengthen the thermowell life during operations and help minimize maintenance-related reactor shutdowns. It should be noted that this committee was told during its data gathering that increasing the diameter of the thermowells would require new holes to be drilled into the SCWO reactor heads, which would necessitate conducting new pressure assessments on the heads, taking considerable time. This committee was also told that, were thermowell thickness to be increased for only the portion that extends into the reactor below the head, the reactor would have to be opened to replace the thermowells. This may increase the complexity, and perhaps the time required for change-out, of the thermowells. At the present time, the thermowells can be replaced through the reactor head without opening the reactor.[11]

Thermowell thinning is also observed to have the characteristics of erosion, so another way to address the corrosion of thermowells could be by reducing the feed velocity, although that would affect processing rates (NRC, 2013). Still, with a minimum required overall availability of only 55 percent, as discussed in the "Processing Rates, Availability, and Processing Parameters" section, there may be room in the operations schedule to accommodate lower feed rates.

From a safety perspective, if the replacement of the thermowell is more frequent than what is prescribed, workers would be exposed more frequently to the hazards identified in the "Safety, Risk Assessment, and Risk Management" section of this report.

Finding 9. It may be possible to extend thermowell life by using thicker thermowells in the SCWO reactors. Thermowell erosion and corrosion could also be mitigated by reducing the flow rates in the SCWO reactors. The relative processing rates of the agent neutralization reactors, the SCWO, and the capacity of the hydrolysate storage tanks may afford sufficient slack to accommodate slower feed rates. If thermowell lifetimes could be extended to a period of time comparable to that of the liners, there would be a significant reduction in required maintenance.

Recommendation 8. BGCAPP staff should seriously consider using thicker thermowells in the SCWO reactors and should explore the possibility of reducing SCWO feed rates while still maintaining adequate availability to not affect BGCAPP main plant operations.

[11] G. Lucier, deputy chief scientist, BGCAPP, "Supercritical Water Oxidation (SCWO) Update Briefing," presentation to the committee, January 14, 2019.

Correlation of Change-Out Frequencies and Corrosion Rates

The liner and thermowell change-out frequencies can be correlated with reactor availability and corrosion rates. These values can be used to infer metrics that might have utility for evaluating reactor performance. The current operational schedule for GB assumes 75 hr of operating time between thermowell change-outs, and 300 hr of operating time between liner change-outs (Figure 1). Thermowell change-outs were conservatively estimated to require 6-7 hr, while liner change-outs are estimated to require 12 hr.

Figure 1 shows that over the course of a 333 hr cycle, there is one combined liner and thermowell change-out and there are three separate thermowell change-outs. The total time to accomplish all of these change-outs is 33 hr. This means that SCWO operating time accounts for 90 percent of the 333 hr cycle, corresponding to a 90 percent availability.

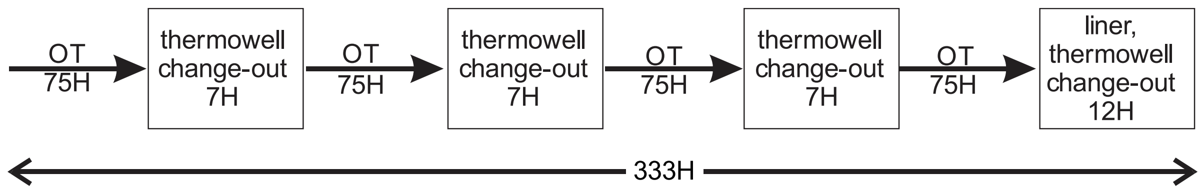

FIGURE 1 Timeline for thermowell and liner change-outs, based on a 90 percent SCWO reactor availability. NOTE: OT, operating time. SOURCE: Committee generated.

The extent of corrosion can be calculated based on 300 hr operating time and a corrosion rate of 1.1 mil/hr (this rate was measured for the 100 hr GB performance test conducted as part of the FOAK testing [NRC, 2013]), resulting in a value of 330 mil of corrosion over the course of 300 hr. This is very nearly equivalent to the maximum allowable extent of corrosion, which is specified in the system design as 67 percent of the original liner thickness. This is equivalent to 335 mil of corrosion for a liner having a starting thickness of 500 mil.

This information can be used to back-calculate the corrosion rate that would cause the availability to drop below the minimum acceptable value of 55 percent

$$\text{availability} = 0.55 = \left(\frac{4\text{OT}}{(4\text{OT} + 33)}\right),$$

where OT is the operating time between successive thermowell change outs, 4OT represents the operational lifetime of a liner, and 33 is the total time in hours required for the change out of the thermowells and the liner. Solving this expression algebraically for OT results in an operating time value of 10.1 hr, and the corrosion rate that would result in loss of 335 mil of liner material would be 8.3 mil/hr:

$$\text{corrosion rate} = \left(\frac{335\ \text{mil}}{4 \times 10.1\ \text{hr}}\right) = 8.3\ \text{mil/hr}\ .$$

This calculated corrosion rate provides a value against which to compare corrosion rates calculated from extent of corrosion measurements made at local positions in the liner to see if availability can be expected to drop below 55 percent. Performing this calculation for the design basis of 76 percent availability gives a corrosion rate of 3.2 mil/hr.

It should also be noted that the shorter operating time value of 10.1 hr implies that the frequency of liner change-out is increased. In calculating the above estimates for OT value and corrosion rate, it was assumed that the frequency of thermowell replacement also increased proportionally with the liner replacement frequency.

These estimates suggest performance metrics for the corrosion rate, which are presented in Table 7, below. The point to be emphasized here is that these metrics assume a uniform corrosion mechanism. However, in addition to uniform corrosion, BGCAPP may well find local corrosion (pitting or cracking), which are modes of corrosion that are not well represented by the uniform corrosion estimates made above. Therefore, corrosion rates are informative but are not fully diagnostic of the way the materials of construction will perform. Another way to look at this is to recognize that cracks or pitting could occur in circumstances where the uniform rates are acceptably low, but localized penetration rates may be unacceptably high. What this situation underscores is the need for BGCAPP to evaluate the performance of the liners during the 6-month initial operating period in which water, surrogate, and then hydrolysate will be evaluated.[12] That approach will provide more confidence in the likelihood that the SCWO system will perform as expected or not, and will demonstrate that the FOAK testing actually does apply.

The committee also notes that failure of the reactor resulting from nonuniform corrosion mechanisms has the potential to cause greater risk compared to uniform corrosion, because of the greater probability of the formation of cracks in the reactor materials. If evidence of nonuniform corrosion, particularly cracking, is discovered while inspecting the reactor or feed lines, this finding would correlate with a value of 3 ("success unlikely") on the graded scale because of the potential compromise to the unit safety envelope.

Perhaps more likely is the possibility that an increased corrosion rate would result in lowered processing rates for the hydrolysate, which would compromise agent processing and scheduling success. The reactor availability that would correlate with such a compromise has been estimated at 55 percent, which would correspond to a liner change-out period of ≤40.3 hr and a thermowell change-out period of ≤10.1 hr. The committee notes that in the event of decreased reactor availability resulting from shorter liner and thermowell operating times, technical solutions to the corrosion problems may well be available, but that the impact on schedule may make the performance unacceptable. A SCWO availability of <55 percent would extend the completion date beyond the December 2023 target date, which would be an administrative failure, not a technical failure, of the project.

The corrosion rates measured using VX hydrolysate in the FOAK tests were less variable compared to those for GB (NRC, 2013). The average corrosion rate for all of the VX hydrolysate tests was 1.2 mil/hr, modestly higher compared to the 1.1 mil/hr used for GB in the above evaluation. However, the corrosion rate that would result in <55 percent availability is still 8.3 mil/hr in both cases, because it is based on the times to change the thermowell and the liner, which are used to calculate operational time between the change-out events. Table 7 proposes some metrics in this area.

Water Recovery System Considerations

This section addresses goals 11-13 in the list of effectiveness goals in Table 1. The SCWO units were originally conceived to operate in tandem with the WRS. The WRS consists of three SCWO effluent storage tanks, a conventional pretreatment system, three spiral wound RO units, and storage tanks used to hold RO permeate (NRC, 2013). This system is designed to separate liquid effluent from the SCWO into RO permeate, which is principally water, and a brine, which is referred to as RO rejectate.

An objective of BGCAPP is to minimize the use of water during operations, and one approach is to use the RO permeate to quench the SCWO reaction occurring at the outlet of the SCWO reactor. In order to function in this capacity, the WRS needs to meet two criteria: (1) the RO permeate to be used as quench water for SCWO should contain no more than 500 mg/L total dissolved solids, and (2) the system must generate sufficient recycled RO water to meet SCWO quench water needs (NASEM, 2015).

[12] After the report had been completed, PEO ACWA decided to shorten the 6-month preoperational testing period to a yet-to-be-determined span. The report does not reflect this change.

The committee expects that the RO system will be able to easily achieve the design objective of <500 mg/L total dissolved solids, and that this risk will be mitigated during planned operational testing (NASEM, 2015; NRC, 2012). The WRS will be operated together with the SCWO during 1,200 hr of simulant-based testing that is being planned, which is expected to provide data and operating experience enabling evaluation of the performance and reliability of the WRS.[13]

TABLE 7 Proposed Corrosion Metrics

Graded Scale	Definition	Safety	Performance	RAM
0	Maximum liner corrosion rate is <1.1 mil/hr.	No impact	No impact	No impact
1	Maximum liner corrosion rate is between 1.1 mil/hr and 8.3 mil/hr.	Increased change-out frequency and related system shutdown required; worker safety becomes increasingly of concern.	Effect on performance indeterminate. Likely no impact; however, presence of increased TiO_2 may affect eutectic composition and behavior.	Increased impact on availability, but still less than minimum acceptable values.
3	Maximum liner corrosion rate is ≥8.3 mil/hr (i.e., liner replacement more frequently than on 40 hr intervals).	Significantly increased change-out frequency and system shutdown required; worker safety becomes increasingly of concern.	Effect on performance indeterminate. Higher likelihood that increased TiO_2 will affect eutectic composition and behavior. Technical solutions exist but will compromise performance and scheduling success.	Significant impact, with availability now less than the minimum acceptable value of 55 percent. Technical solutions exist but will compromise performance and scheduling success.
3	Thermowell replacement more frequently than on 10 hr intervals.	System shutdown required; worker safety becomes increasingly of concern.	Technical solutions exist but will compromise performance and scheduling success.	Technical solutions exist but will compromise performance and scheduling success.
3	Nonuniform corrosion, or cracking, of reactor or feed line materials.	Unknown serious flaws induced by the supercritical or high-subcritical environment may cause a breach of the SCWO reactor or feed lines.	Potential for significant impacts on performance from failure of reactor vessel or feed lines, resulting in unplanned and unaccounted throughput reductions.	Significant impact from the inability to predict reliably reactor component service life.

[13] Ibid.

Evaluation of whether or not the WRS will produce sufficient RO water requires a consideration of the demand for water by the SCWO units. The water required by each of the three SCWO trains is projected to be <20 gpm during the GB campaign, while the permeate generated by the two on-line RO units is estimated at 71 gpm (NASEM, 2015). A similar evaluation for the VX campaign also indicates that the WRS should be able to produce all of the quench water demand for the SCWO reactors.

However, PEO ACWA and the committee both acknowledge that an inadequate generation of RO permeate water or a failure of the RO system has the potential to impact the SCWO operations. The possibility that the WRS may not keep up with the SCWO reactors or produce sufficient water for the SCWO quench has motivated the procurement of two water demineralization units, each with a capacity of 60 gpm, which will be sufficient for quenching the SCWO in the event that the RO systems fail to generate enough water.[14] Hence, the demineralization units should be able to provide sufficient water should the performance or availability of the WRS be inadequate.

In summary, it is unlikely that problems with the WRS will adversely impact SCWO operations. It has been noted that an adverse consequence of a WRS failure would be that the volume of wastewater would be significantly greater than initial estimates. Estimates cited in NASEM (2015) are a 15-fold flow increase for the GB campaign, and an 8-fold flow volume increase for the VX campaign. More recent information provided suggests a 3-fold increase in wastewater shipments.[15] While this outcome would not be optimal, the committee does not believe that it would imperil the function of the SCWO units.

SAFETY, RISK ASSESSMENT, AND RISK MANAGEMENT

Safety is paramount for the successful operation of the SCWO, as it is with the entire chemical agent destruction program. The excellent safety program at BGCAPP is evidenced by the plant's participation in the Occupational Safety and Health Administration Voluntary Protection Program, years of operation without a lost time accident, and an extremely low recordable injury rate. This report addresses safety concerns stemming from discussions of SCWO effectiveness goals, and from general overall risk assessment and management discussions.

Based on information provided to the committee, employees reportedly expressed concerns about performing maintenance on one of the three SCWO reactors while one or both of the remaining reactors are operating.[16] Risks associated with performing maintenance while SCWO reactors are operating can be divided into two categories: working within an idle module while one or both of the other reactor modules are operating, and working outside an idle reactor module while one or both of the other reactor modules are operating.

Many methodologies exist to perform risk assessment and management. All require knowledge of the hazards present, assets at risk, impacts should there be a safety compromise or failure, and hazard mitigation approaches. The identified hazards, assets at risk, and impacts are often placed into a variety of matrices that are primarily subjective in nature. However, numbers are sometimes assigned in an attempt to quantify the risk with an appearance of objectivity. This is often accomplished without sufficient data to, for example, determine definitive failure rates, which if available would allow for the accurate quantitative assessment of risks. The point is that risk assessment and management is often a subjective exercise and, to be done right, requires detailed knowledge of many factors specific to the situation being assessed.

[14] Ibid.
[15] Ibid.
[16] Discussions between Candace Coyle, chief scientist, PEO ACWA, and the committee, January 14, 2019.

Major Hazards and Sources of Risk Related to SCWO Reactor Maintenance

The major potential hazards when performing maintenance within the individual reactor modules while one or both of the other reactor modules are operating include

- Failure of a SCWO reactor pressure vessel during operation (i.e., not a reactor liner);
- Failure of a compressed air line in an external operating reactor module; and
- Failure of a high-pressure isopropyl alcohol (IPA) line in an external operating reactor module.

The major potential hazards and sources of risk when performing maintenance outside the reactor modules while one or both of the other reactor modules are operating include

- Failure of a SCWO reactor pressure vessel in an operating reactor module;
- Failure of compressed air lines in an external operating reactor module;
- Failure of high-pressure IPA lines in an external operating reactor module;
- Failure of other feed lines in an external operating reactor module;
- Removal of reactor linings; and
- Removal of the thermowells.

These potential hazards and safety concerns are independent of the five safety issues that the SCWO Working Group identified among its 33 critical deficiencies. The deficiencies identified by the SCWO Working Group are not addressed in this report because the committee believes that they have been adequately considered.

Maintenance Within a Reactor Module While One or Both of the Other Reactor Modules Are Operating

The committee assumes that all sources of energy within an idle module that is being serviced will be locked out by using the established procedures, to include verification; therefore, the potential hazards within the idle module will have been mitigated. Thus, the safety hazards and risks while doing maintenance inside a reactor module are from other operating reactor modules. Should a reactor pressure vessel fail while operating, there could be hazards associated with shrapnel, high-temperature liquids, and exposure to hydrolysate.

The sides of the reactor modules are enclosed by two Lexan panels that are 3/8 in. thick. Lexan is used in bulletproof glass.[17] The arrangement is shown in Figure 2.

When working within a reactor module that is idle (not operating), two such configurations (four Lexan panels total) isolate workers from any incident that would occur within an adjacent operating module (the operating module would also have two Lexan panels). The concern is whether the integrity and strength of the remainder of the enclosure, specifically doors and other access portals, is equal to that of the Lexan panels.

The compressed air line is under approximately 3,500 psi. At this pressure, a total rupture will immediately reduce the pressure to a level that would not have a significant impact on the skin of a worker such as air slicing or puncture; however, shrapnel may pose a hazard. Notwithstanding, it is a best practice for the compressed air line to be locked out and remaining pressure released within the idle module, eliminating this risk, while the impact of an air line rupture within the operational module would be contained within the physical barriers of the module.

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[17] G. Lucier, deputy chief scientist, BGCAPP, "Supercritical Water Oxidation (SCWO) Update Briefing," presentation to the committee, January 14, 2019.

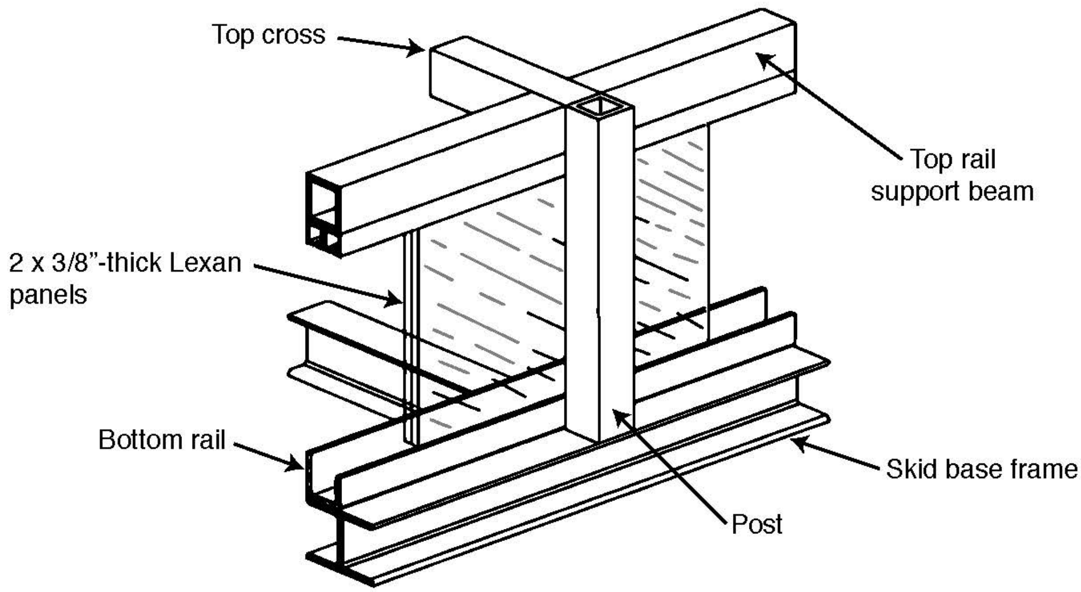

FIGURE 2 Arrangement of Lexan panels enclosing SCWO reactor modules. SOURCE: G. Lucier, deputy chief scientist, BGCAPP, “Supercritical Water Oxidation (SCWO) Update Briefing,” presentation to the committee, January 14, 2019.

The rupture of the IPA line could create a flammable atmosphere within a module. Best safety practices would call for the IPA line to be locked out and remaining contents drained within the idle module, eliminating this risk, while the impact of an IPA line rupture within the operational module would be contained within the physical barriers. The SCWO Process Building fire suppression system and the gaseous hydrocarbon detectors on either end of the reactor modules, which can shut down SCWO operations, are expected to provide the required safety envelope in the event of a fire.

Maintenance Outside a Module

Again, should a reactor pressure vessel fail while operating, there could be hazards associated with shrapnel, high-temperature liquids, and exposure to hydrolysate. When workers perform maintenance outside a reactor module but within the SCWO building, while either both or one of the other modules is operational, the full protection as described above from four Lexan panels will not be present. There will be only two Lexan panels between any catastrophic failure and workers. The concern again is whether the integrity and strength of the remainder of the enclosure, specifically doors and other access portals, is as great as that of the Lexan panels. A key concern is whether the Lexan panels can withstand the energy expended should a SCWO pressure vessel fail.

The compressed air line is under approximately 3,500 psi. At this pressure, a total rupture will immediately reduce the pressure to a level that would not present a significant air slicing or penetration impact on the skin. However, a small hole (leak) in the air line could allow for the air to slice or penetrate skin. If a compressed air line ruptured completely, shrapnel may also pose a hazard.

Gaseous hydrocarbon detectors are installed inside reactor modules on both ends—at the end with the IPA supply and at the end that holds the SCWO reactor—and will activate if the IPA line ruptures and results in a fire. The SCWO Process Building also has a fire suppression system. The established procedures would need to be followed for shutting down the operation of the other reactors.

The rupture of a feed line could result in workers being exposed to the hydrolysates and feed additives. In the case of a feed line rupture, the established procedures would need to be followed for shutting down the operation of the other reactors.

The potential hazards associated with the removal of liners and thermowells are primarily physical—for example, cutting and crush injuries—and would be mitigated by following established procedures. Many of the potential hazards above are also associated with entering an environment where either one or two of the reactor modules are operational during the replacement of a liner or thermowells on an idle reactor. The use of nondestructive testing to gather data on the condition of the SCWO system and its components during startup testing is discussed in the "Hydrolysate Feed to the SCWO Reactors" section. Nondestructive testing could also be used during startup testing to evaluate liner and thermowell corrosion and determine whether it might be possible to reduce liner and thermowell change-out frequencies. If this were possible, it would have the benefit of reducing the safety risks associated with liner and thermowell change-out.

To assess and manage risks, an expanded risk assessment may be considered with the use of objective data where possible, to address the items and areas of concern identified in the list below. Objective data can be obtained during the 6-month operational testing phase by identifying all operating and preventative maintenance issues, regardless of how minor. This data then would need to be analyzed to establish predictive indicators of failure and risks to the employees. Another potential source of useful information is the lessons learned from prior chemical demilitarization operations, both the baseline program, which used incineration, and operations at the Pueblo Chemical Agent Destruction Pilot Plant. For instance, while the BGCAPP SCWO system is fundamentally different from any operations at baseline facilities, there may be useful experience from those facilities in general industrial process safety and specific situations encountered. Lessons from the Pueblo plant in hydrolysate handling might also be similarly useful and more directly applicable. The factors to be included in any safety and risk management include the following:

- Searching for and applying relevant lessons learned from previous chemical demilitarization operations that might be useful in the context of BGCAPP SCWO operations.
- Establishing an in-depth training approach to alleviate fears of the unknown and to assist in the development of detailed standard operating procedures to mitigate or lessen the impact of the identified potential hazards.
- Ensuring that the entire reactor modules provide the same level of protection as the Lexan panels. Special considerations need to be given to doors and other closable openings.
- Calculating the energy of projectiles should an explosion within a module occur to ensure that the enclosure will contain all projectiles.
- Exploring the possibility of using in situ nondestructive testing for the liners of the reactors to possibly minimize change outs.

STOP-WORK AND NO-GO SITUATIONS

The third list item in the statement of task above calls for the committee to "Identify any 'no-go' or 'stop-work' factors (e.g., safety) that would result in an immediate halt of BGCAPP SCWO operations." In the course of its data gathering and consideration of the information received, the committee found only two types of event that had the potential to result in no-go or stop-work decisions.

The committee believes that any technical issue could be resolved with adequate time and money. Even something as significant as the failure of a major piece of process equipment for which there is no spare could be overcome. It became clear to the committee that PEO ACWA's decision criteria are mainly based around considerations of program schedule and budget, in addition to treaty compliance requirements and a consideration of the positions of public interest groups around BGCAPP. The committee believes that only PEO ACWA can appropriately determine the point at which technical problems become so expensive or cause so much delay that it makes sense to halt SCWO operations. However, the committee can point out where it believes technical problems could have a significant impact on schedule, and it does so, which should help inform PEO ACWA in its decision making regarding SCWO operations.

From a safety perspective, the committee identified two "no-go" or "stop-work" possibilities. The first, given in Table 5, would be if aluminum levels in hydrolysate feeds spiked to over 500 ppm in individual batches. The safety concern here is the clogging of safety-related equipment such as pressure relief valves. The second would be a compromise to the unit safety envelope resulting from a failure of the air, IPA, or hydrolysate supply lines or failure of the SCWO reactor vessel (see the "Corrosion" section, above).

BGCAPP appears to have well-developed safety procedures and safety considerations as part of the design of this high-pressure, high-temperature system. Still, the committee envisions three possible safety scenarios that could lead to significant concerns. The impact of these safety concerns is a judgement best made by PEO AWCA. One concern is the full development of safety procedures when performing maintenance operations on one SCWO train while at least one other SCWO train is in operation. The committee believes that a more thorough analysis of safe operating procedures given the proximity of the SCWO reactor trains as they were installed in the BGCAPP facility would address this. A second concern is the inexperience of all shifts of BGCAPP staff. The SCWO Working Group has established a comprehensive training plan, but its operating procedures would benefit from significant leader follow-up checks to help prevent human error due to initial inexperience with this complex system. The third concern is the potential second- and third-order effects of unforeseen events that may develop when processing actual hydrolysate. The committee believes that the current SCWO system has sufficient safety design features such as control systems for pressure buildup, but unforeseen events may cause some of this equipment to malfunction (e.g., solid buildup on a pressure relief valve may prevent its safe operation). If the concerns above are properly addressed, the committee believes that safety-related stop-work events can be prevented.

Finding 10. A more thorough analysis of safe operating procedures for conducting maintenance operations in the presence of operating SCWO reactors, rigorous management of the staff as it gains experience, and efforts to address concerns about unforeseen safety events discussed in this report could minimize or prevent stop-work safety events.

Recommendation 9. The BGCAPP staff should conduct a more thorough analysis of safe operating procedures for conducting maintenance operations in the presence of operating SCWO reactors; should apply any useful lessons learned from prior chemical demilitarization experience to SCWO operations and maintenance; should ensure rigorous management of the staff as it gains experience, such as leader follow-up checks; and should address concerns about unforeseen safety events to minimize or prevent stop-work safety events.

There are occurrences that might necessitate short-term suspension of SCWO operations. One could be if salts and solids build up in the SCWO reactors and downstream systems, causing plugging. While the likelihood of this occurrence is low, based on extensive BGCAPP testing and experience, uncertainty in the composition of the actual hydrolysate and effects of these variations on processing, the actual behavior of the hydrolysate-based eutectic salt mixture, or human error could lead to nonideal conditions of solids accumulation. Another occurrence would be if corrosion were unexpectedly severe, and certainly if a liner were breached. These occurrences could indicate that the chemistry and fluid dynamic behavior of the feed is significantly different from what was expected, and a short-term stop in operations might be warranted to understand what is happening. Repeated unexplained system shutdowns might also indicate a need for a short-term stop to SCWO operations to determine the causes and attempt remediations. At what point these types of events might warrant a long-term suspension of SCWO operations is, again, a decision for PEO ACWA.

Sincerely,

Gary S. Groenewold, Chair
Committee on Metrics for Successful Supercritical Water Oxidation System Operation at the Blue Grass Chemical Agent Destruction Pilot Plant

Attachments:
A—Roster and Biographical Information
B—References
C—Acronyms
D—Acknowledgment of Reviewers

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Attachment A

Roster and Biographical Information

ROSTER OF THE COMMITTEE ON METRICS FOR SUCCESSFUL SUPERCRITICAL WATER OXIDATION SYSTEM OPERATION AT THE BLUE GRASS CHEMICAL AGENT DESTRUCTION PILOT PLANT

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BIOGRAPHICAL INFORMATION

GARY S. GROENEWOLD, *Chair*, is a senior scientist in the Energy and Environment Directorate at the Idaho National Laboratory, where he has conducted research in surface chemistry, gas-phase chemistry, and analytical measurement since 1991. His research has focused on determining speciation and reactivity of radioactive and toxic metals (U, Np, Pu, Hg), and of toxic organic compounds (including VX, mustard, and sarin). Dr. Groenewold received a Ph.D. in chemistry from the University of Nebraska in 1983, where he studied ion molecule condensation and elimination reactions under the direction of Dr. Michael Gross. He has authored more than 130 research articles in these areas, and has served on several ad hoc committees for the National Academies of Sciences, Engineering, and Medicine. Dr. Groenewold has served on seven chemical demilitarization committees and is thoroughly informed on the issues at Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP) and the concerns about the supercritical water oxidation (SCWO) system.

RONALD M. BISHOP is founder of AEHS, Inc., and president of A.H. Bishop and Associates. Both corporations provide environmental, health, and safety consulting services and training. He earned his bachelor's of science degree in preventive medicine (environmental health engineering) from the University of Washington and a master's of public health in industrial hygiene with additional concentration in air pollution from the University of Minnesota. Mr. Bishop also served for 2 years as director of the Office of Safety and Health Protection at the Oak Ridge National Laboratory, where he was responsible for all safety, industrial hygiene, Occupational Safety and Health Administration (OSHA), hazardous waste management, and technical training. Mr. Bishop spent 25 years in the U.S. Army with numerous environmental, safety, and health positions, retiring as a Colonel; his last assignment was commander of the U.S. Army Environmental Hygiene Agency. He has worked 20 years

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as an environmental, safety, and industrial hygiene consultant. Mr. Bishop also provides instruction for a myriad of courses, including indoor air quality, asbestos, lead, respiratory protection, LO/TO, HAZCOM, confined space, and OSHA's 501 Voluntary Compliance.

RUSSELL P. LACHANCE is an associate dean and an associate professor of chemical engineering at the U.S. Military Academy. His active areas of research include waste-to-energy research and chemistry and chemical engineering education. His work in SCWO includes the modeling of oxidation and hydrolysis reactions in supercritical water-free radical elementary reaction networks and their applications, the co-oxidation of methylphosphonic acid and ethanol in supercritical water, and thermochemical biofuel production in hydrothermal media. Dr. Lachance earned a B.S. with a chemistry concentration from the U.S. Military Academy, an M.S. in chemical engineering from the Massachusetts Institute of Technology (MIT), and a Ph.D. in chemical engineering, also from MIT. He is retired from the Army with the rank of Colonel.

RONALD M. LATANISION is the corporate vice president at Exponent, Inc. Prior to joining Exponent, Dr. Latanision was the director of the H.H. Uhlig Corrosion Laboratory in the Department of Materials Science and Engineering at MIT, and held joint faculty appointments in the Department of Materials Science and Engineering and in the Department of Nuclear Engineering. He is now an emeritus professor at MIT. In addition, he is a member of the National Academy of Engineering and a fellow of ASM International, NACE International, and the American Academy of Arts and Sciences. Dr. Latanision's research interests are focused largely in the areas of materials processing and in the corrosion of metals and other materials in aqueous (ambient as well as high temperature and high pressure) environments. He specializes in corrosion science and engineering, with particular emphasis on materials selection for contemporary and advanced engineering systems, and in failure analysis. His expertise extends to supercritical water power generation and waste destruction. Dr. Latanision's research interests also include stress corrosion cracking and hydrogen embrittlement of metals and alloys, water and ionic permeation through thin polymer films, photoelectrochemistry, and the study of aging phenomena/life prediction in engineering materials and systems. He speaks annually at the MIT Reactor Technology Conference for Utility Executives. Dr. Latanision is a member of the International Corrosion Council and serves as co-editor-in-chief of *Corrosion Reviews*, with Professor Noam Eliaz of Tel-Aviv University.

MURRAY GLENN LORD is associate director of Environmental Health and Safety and director of the Operations Technology Center at Dow Chemical Company. He is responsible for the research program for technology development for Global Environmental Operations, which includes project areas in process optimization, technology development, and capital project execution. Mr. Lord has experience in project areas across multiple business and technology areas and has experience in starting up and operating industrial processes. He has served on three past chemical demilitarization committees of the National Academies, including the 2015 Committee on the Review Criteria for Successful Treatment of Hydrolysate at the Pueblo and Blue Grass Chemical Agent Destruction Pilot Plants, which authored the report that serves as the basis for the current report, and the 2013 Committee on Assessment of Supercritical Water Oxidation System Testing for the Blue Grass Chemical Agent Destruction Pilot Plant. He is also a member of the standing Committee on Chemical Demilitarization.

Attachment B

References

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Attachment C

Acronyms

AFS	aluminum filtration system
APS	aluminum precipitation system
BGCAPP	Blue Grass Chemical Agent Destruction Pilot Plant
FOAK	first-of-a-kind
IPA	isopropyl alcohol
PEO ACWA	Program Executive Office for Assembled Chemical Weapons Alternatives
RAM	reliability, availability, and maintainability
RO	reverse osmosis
SCWO	supercritical water oxidation
TOC	total organic carbon
WRS	water recovery system

Attachment D

Acknowledgment of Reviewers

This Consensus Study Report was reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise. The purpose of this independent review is to provide candid and critical comments that will assist the National Academies of Sciences, Engineering, and Medicine in making each published report as sound as possible and to ensure that it meets the institutional standards for quality, objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process.

We thank the following individuals for their review of this report:

Glen T. Daigger, NAE,[1] One Water Solutions, LLC,
Richard C. Flagan, NAE, California Institute of Technology,
Stephan C. Graham, Army Public Health Center (retired),
Igor Novosselov, University of Washington, and
Robert B. Puyear, Independent Consultant.

Although the reviewers listed above provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations of this report nor did they see the final draft before its release. The review of this report was overseen by M. Granger Morgan, NAS,[2] Carnegie Mellon University, and Hyla S. Napadensky, Napadensky Energetics, Inc. (retired). They were responsible for making certain that an independent examination of this report was carried out in accordance with the standards of the National Academies and that all review comments were carefully considered. Responsibility for the final content rests entirely with the authoring committee and the National Academies.

[1] Member, National Academy of Engineering.
[2] Member, National Academy of Sciences.